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Air Pollution Impacts When Quenching Blast Furnace Slag with Contaminated Water

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AIR POLLUTION IMPACTS WHEN QUENCHING BLAST FURNACE SLAG WITH CONTAMINATED WATER

by

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16. ABSTRACT The report gives results of an effort to determine if a potential alternative to treatment prior to discharge of coke plant wastewater will result in a significant increase in emissions to the atmosphere. The alternative is using the wastewater, untreated, to quench blast furnace slag. To develop a preliminary determination, six emission measurements were made on a laboratory-scale facility simulating typical slag quenching practice. Test parameters encompassed two slag temperatures (594 and 816 C) and two waters, ASTM Type 1 water and coke plant effluent diluted to 2500 mg/liter TDS. The results indicate that particulate emissions increase with slag temperature and TDS in the water. Minor quantities of organic compounds were emitted, but showed no correlation with test variables. The data also showed no correlation between emissions of sulfur dioxide or fluoride and test variables.

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Pollution	Coking	Pollution Control	13B
Slags	Particles	Stationary Sources	11F, 11B
Blast Furnaces	Dust	Slag Quenching	11G
Quenching (Cooling)		Particulate	13H
Waste Water	Aerosols		07D
Contamination			14G

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ABSTRACT

A potential alternative to treatment prior to discharge of coke plant waste waters is to use it, untreated, to quench blast furnace slag. The question arises, will this result in a significant increase in emissions to the atmosphere. To develop preliminary answers to this question, a series of six emission measurements were made on a lab-scale facility simulating typical slag quenching practice. Test parameters encompassed two slag temperatures (1100°F and 1500°F) and two waters, ASTM Type 1 water and coke plant effluent diluted to 2500 mg/l TDS. The results indicate that particulate emissions increase with slag temperature and TDS in the water. Minor quantities of organic compounds were emitted but showed no correlation with test variables.

The data also showed no correlation between emissions of sulfur dioxide or fluoride and test variables. This project was a continuation of earlier work reported in EPA-600/2-84-072.

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The PEI Project Director was R. W. Gerstle, the Senior Reviewer was William Kemner, and the Project Manager was Gopal Annamraju. Gopal Annamraju and P. J. Schworer were the primary authors of the report.

SECTION 1

INTRODUCTION

This report describes the results of an experiment conducted to evaluate the impact of atmospheric emissions from quenching blast furnace slag with contaminated water. The work was sponsored by the Air & Energy Engineering Research Laboratory (AEERL of the U. S. Environmental Protection Agency (EPA) at Research Triangle Park, North Carolina, in support of EPA's Effluent Guidelines Division. This task is a continuation of similar work[1] performed by PEI Associates, Inc., in the Fall of 1982. The work involved an assessment of atmospheric emissions from quenching of blast furnace slag with blast furnace blowdown water.

This study involved a laboratory scale assessment of simulated slag quenching in a specially designed pot partially filled with fresh molten slag, reheated in a propane-fired furnace, and quenched with blast furnace blowdown water. This study revealed a direct relationship between the content of total dissolved solids (TDS) in the quench water and the resultant level of particulate emissions. A direct relationship was also found between the slag temperature and particulate emission rates. Based on the limited data obtained in this work, no correlation could be drawn between slag temperature or level of specific contaminants in the quench water and the resulting air emissions of that contaminant. The purpose of the current assignment was to expand the data base by measuring atmospheric emissions during blast furnace slag quenching with very clean water and with contaminated water. Laboratory scale equipment assembled for the previous study was used in the current study.

Slag was poured into the slag pots at the blast furnace and transported to the experimental furnace. Blowdown water was obtained from another blast

furnace with a moderately tight recycle system and transported to the laboratory in 5-gallon jars. Coke plant wastewater obtained from a coke plant was diluted to ≅2500 mg/liter of total dissolved solids (TDS) and used for quenching. ASTM Type I water with low TDS and no organics was used as a baseline for comparison. A series of six test runs was conducted at two different ranges of slag temperature. These tests provided a qualitative estimate of emissions under different slag temperatures and the effect of the use of different types of water on these emissions.

Section 2 describes the test plan and presents the specific approach adopted, the equipment design, and the test design. Section 3 describes the test procedure and presents the analytical data. Section 4 presents an evaluation of the test data. Section 5 presents the conclusions and recommendations.

SECTION 2

TEST PLAN

2.1 BACKGROUND

The use of blast furnace blowdown water to quench hot blast furnace slag provides an inexpensive method of blast furnace wastewater treatment that consumes the water and thus prevents pollutant discharge to receiving streams. The energy that produces this evaporation of the wastewater is available in the hot slag but is not generally utilized at the plant. This alternative is not without possible detrimental effects, however. Previous EPA tests of coke quenching with quench water containing high levels of dissolved solids show that such practices tend to generate high levels of fine particulate air emissions.[2,3] Also, other contaminants in the blowdown water could vaporize, break down, or recombine to create undesirable air pollutants. Data are needed concerning the possible adverse environmental effects of slag quenching with blast furnace blowdown water. Demonstrating that blast furnace blowdown wastewater can be used for slag quenching without detrimental environmental effects would allow the Best Available Technology (BAT) limitations for this category to be implementd at a decreased cost.

As discussed in Section 1, a laboratory scale assessment of simulated blast furnace slag quenching with mill service water and blast furnace blowdown water was conducted by PEI[1]. The results indicate a direct relationship between the total dissolved solids (TDS) content of the water used to quench blast furnace slag and the resultant level of particulate emissions released to the atmosphere. A direct relationship was also found between the temperature of the slag and prticulate emission rates. Other than particulate emissions, no correlation was apparent between slag temperature or level of specific contaminants in the quench water and the resulting air emissions of that contaminant.

In further work performed under this project, blast furnace slag was quenched with clean water and other contaminated waters using the laboratory scale equipment assembled for the previous project; the resulting air emissions were then measured.

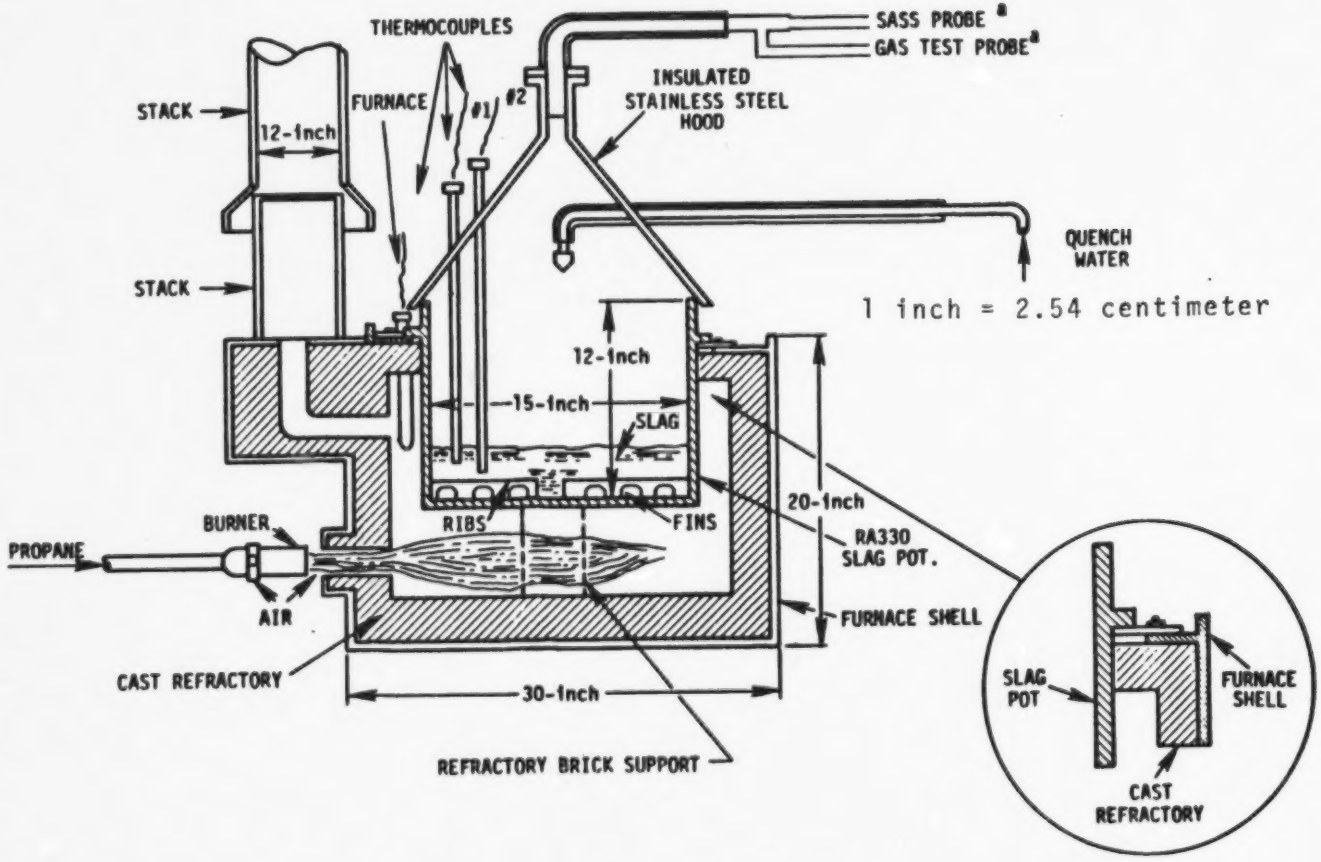
The previous experiments used a specially designed container partially filled with blast furnace slag that was reheated in a custom-designed furnace with a propane burner. After the bulk slag reached the desired temperature, the test water was continuously evaporated on the slag surface while the desired bulk slag temperature was maintained. The emissions that evolved along with the steam were captured for analysis.

2.2 EQUIPMENT DESIGN

Figure 2-1 shows the general arrangement of the slag container, furnace, and the experimental setup. The main components of this setup are the slag pot, furnace, hood, burner, and water inlet pipe, which are described here. The same setup used previously for evaluating slag quenching with BF blowdown water was used with minor modifications.

Slag Pots

The slag pots had to withstand severe thermal stress because of continuous heating over 4 to 6 hours and simultaneous quenching of the surface of the slag inside the pot. The pots also had to withstand repeated handling and high temperatures from direct contact with molten slag. Therefore, 3/16-in.-thick RA-330 (a high-temperature stainless steel with a high percentage of nickel and chromium) was selected for this purpose. Dimensions of the slag pot were 38-cm (15-in.) i.d. by 30 cm (12 in.) in height. The bottom of the pot was reinforced with pie-slice ribs, which also aided in heat transfer to the slag. Additional fins were provided for better heat transfer. A 1.27-cm (1/2-in.)-wide flange was welded around the circumference of the pot [9 cm (3.6 in.) below the top] to hold it in the furnace. Three identical pots were custom-made for this project by Deltec, Inc., a Cincinnati engineering firm. Two adjustable support collars (10-gauge 304 stainless) were made for additional support to the pot when it was inside the furnace.



[a] The Probe not in use will be sealed with a glass socket.

Figure 2-1 General arrangement of the experimental setup (not to scale).

Furnace

The crucible-type furnace with a full cast refractory was custom-manufactured by Frank Schaeffer Co., a Cincinnati engineering firm. The burner port was arranged tangentially so that hot gases swirled around the pot and exhausted from a side flue close to the top of the furnace. The furnace was portable and was set on top of an adjustable scaffolding during the experiments. The combustion gases exited through a small stack and were cooled by dilution air. The hot exhaust gases were exhausted through a chimney, as indicated in Figure 2-1.

Emission Capture Hood

The emission capture hood was made out of 1.6-mm (1/16-in.)-thick 304 stainless steel. The 43-cm (17-in.) diameter at the bottom of the hood allowed for an overhang of around 5 cm (2 in.) when placed over the slag pot. Dilution air entered the hood through a gap between the hood and slag pot. This dilution air served as a carrier gas for the water vapor and emissions and provided a measurable quantity of gas to pass through the Source Assessment Sampling System (SASS) train. The connecting pipe between the hood and the probe was also made of stainless steel.

Probes

Two special probes were attached to the connecting pipe from the emission collection hood. The probes were glass-lined and equipped with the necessary electrical heating arrangements. One probe was connected to the SASS train and the other was used to collect other gases. The probe not in use was sealed off with a glass socket.

Burner

A propane burner was designed in-house for use in the furnace. This modified burner was able to attain high temperatures and provided the clean combustion of propane.

Thermocouples

A thermocouple in a metal sheath was used for continuous measurement of the furnace temperature. Two flexible thermocouples were used to measure slag temperature at two different depths in the slag layer: 1.25 and 3.8 cm (½ and 1½ in.) deep.

Water Inlet Pipe

A stainless-steel inlet pipe with a cooling water jacket was used to transport blowdown water. This arrangement was selected to ensure that the blowdown water did not evaporate before hitting the hot slag. On the basis of previous test runs, however, evaporation was not a problem and hence, water cooling was discontinued for these runs.

Other Equipment

In addition to the equipment described, a special glass filter assembly was designed to hold a 15.24-cm (6-in.)-diameter Whatman filter paper in the SASS train. Other equipment included five-gallon glass jars, Teflon tubing, a 1/3-hp mixer, water pump, and various glassware fittings.

2.3 TEST DESIGN

The main objective of the test series was to evaporate various contaminated waters on the hot blast furnace slag and correlate air discharges and slag characteristics as a function of quench water quality and slag temperature.

The baseline water was ASTM Type I pure water free from any organics and low TDS. The baseline pure water sample was distilled in PEDCo laboratories.

The blast furnace blowdown water also was obtained in 18.9-liter (5-gallon) glass jars from the Middletown works of Armco. The measured TDS content was 1290 mg/liter. The blast furnace wastewater treatment system uses moderately tight recycle.

The untreated coke plant wastewater was obtained from another coke plant in 5-gallon jars. The raw water was analyzed for TDS content and then diluted to $\tilde{=}$2500 mg/liter TDS content by the addition of pure water (ASTM Type I). This diluted coke plant wastewater was used for quenching the BF slag.

Two slag temperature ranges were selected for these tests. The thermocouples were arranged to measure the temperature 12.7 mm and 38 mm (1/2 in. and 1-1/2 in.) below the slag surface. The low-temperature range selected was 538° to 593°C (1000° to 1100°F), and the high-temperature range was 815° to 871°C (1500° to 1600°F), as measured by the thermocouple 12.7 mm (1/2 in.) below the slag surface.

Table 2-1 shows the sequence of sampling runs, quench water type, and slag temperature.

Slag samples were obtained from the Armco Hamilton blast furnaces in batches of three. After the pots were thoroughly cleaned, they were taken to the blast furnace cast house, where a slag spoon was used to remove molten blast furnace slag from the slag runner during a cast. The removed slag was poured into each pot one spoonful at a time and allowed to solidify. This process was repeated until a depth of 6 to 7.5 cm (2-1/2 to 3 in.) was reached [around 11.4 to 13.6 kg (≅ 25 to 30 lb of slag)]. The pots were then allowed to air cool before being transported to the laboratory. The pots were kept covered to avoid any contact with moisture until the time of the test.

In the test approach selected, the slag was heated in the pot to the predetermined temperature and maintained at that temperature while the slag surface was being quenched. The emissions and steam generated during the quench were collected. This prolonged quenching period at a desired temperature allowed collection of a large volume of emissions. The extended sampling period was required because of the expected low concentrations of trace metals and organics. The general arrangement of the test setup is shown in Figure 2-1.

Each test used approximately 15 liters (4 gallons) of the specified type of quench water. During the entire period of each test, the water in the jar was kept under agitation by using a 1/3-hp mixer with a Teflon paddle to ensure solids would not settle out in the jar. A spray nozzle was installed to provide uniform application of quench water to the slag.

Air Sampling Approach

Steam and emissions generated from slag quenching were sampled and analyzed for various pollutants. Two tests were conducted on each type of quench water to determine the composition of the emissions generated at two ranges of slag temperatures. Table 2-2 shows the species sampled, the sampling methods, and analytical procedures followed during the test series. The sampling and analytical procedures are described briefly here.

TABLE 2-1. SAMPLING SCHEME

Test run No.	Quench water type	Slag temperature, °C (°F)
1	ASTM Type I	593 (1100)
2	ASTM Type I	816 (1500)
3	Blast furnace blowdown (TDS ~1250 mg/liter)[a]	593 (1100)
4	Blast furnace blowdown (TDS ~1250 mg/liter)	816 (1500)
5	Coke plant wastewater[b] (TDS ~2500 mg/liter)	593 (1100)
6	Coke plant wastewater[b] (TDS ~2500 mg/liter)	816 (1500)

[a]TDS - Total dissolved solids measured in mg/liter.

[b]The coke plant wastewater TDS will be adjusted to ≅2500 mg/liter by adding ASTM Type I water.

TABLE 2-2. SAMPLING METHODS AND ANALYTICAL PROCEDURES FOR AIR SAMPLES

Species	Sampling method	Analytical procedure
H_2O	SASS	Gravimetric
SO_2	SASS	EPA Method 6
F^-, Cl^-	EPA Method 13B	EPA Method 13B
CN^-	EPA Method 13B	808[4]
NH_3	Impinger train	801[4]
Particulates	SASS	EPA Method 5 (front-half only)
Volatile organics (C_1 to C_7)	Grab samples	GC/FID
Organics	SASS	Modified Level 1
Metals	SASS	ICP[5]

A modified Source Assessment Sampling System (SASS) train was chosen as the principal collection device for three reasons: 1) the sampling rate can be varied up to approximately 114 liters/min (4.0 ft^3/min), 2) a larger sample volume can be collected, and 3) the sampling train is designed to maintain a high temperature of 205°C (400°F). The SASS train was operated without cyclones. The only modifications to the SASS train were a glass-lined probe and glass filter holder, which significantly improved sample quality especially for trace element determinations. The SASS train was operated for approximately 4 hours per run.

One SASS run was conducted for each slag temperature quench with ASTM Type I water, blast furnace scrubber blowdown water, and coke plant wastewater diluted to ≅2500 mg/liter TDS. The filter and front-half rinse for each SASS sample run were gravimetrically analyzed to determine the filterable particulate concentration.

Trace element analysis was performed separately on the front half and back half of one SASS sample run at a given test condition. The analysis was performed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP) to measure the quantity of approximately 40 elements.

For each SASS sample, the various fractions (probe rinse and filter, XAD-2 resin, back-half module rinse, and aqueous condensate) were analyzed separately for organic species according to Level 1 assessment procedures , using low-resolution Gas Chromatography/Mass Spectrometry (GC/MS) analysis for priority pollutants (excluding pesticides and PCBs), Total Chromatographible Organic (TCO) analysis for compounds C_7-C_{16}, and gravimetric analysis for total organics.

Each quench condition was tested once to collect chloride, fluoride, cyanide, and ammonia samples. A total of six samples of each species was collected.

Chlorides, fluorides, and cyanides were determined by use of a modified Method 13B sampling train. Sodium hydroxide was placed in an impinger immediately after the backup filter to capture all the cyanides present in the gas stream.

Ammonia (NH_3) was determined by use of a modified EPA Method 5 sampling train. The impinger solution was 0.1N sulfuric acid instead of IPA and H_2O_2.

Grab samples were collected in Tedlar bags. Aliquots from the bag samples were injected into the GC with the use of a gas sample loop and a 10-port gas switching valve.

Gas samples were collected and analyzed periodically during each quench for volatile organics (C_1-C_7, boiling point range from -160°C to +100°C) by use of a gas chromatograph (GC) with a flame ionization detector (FID) and by following the specified procedures.[3]

Water Samples

Prior to test runs, each water type was analyzed for total dissolved solids (TDS) to ensure proper water quality. In addition one composite sample of each water type was analyzed for organic and inorganic priority pollutants (excluding pesticides and PCBs), TCO, and gravimetric analysis for total organics and metals (≅40 elements by ICP).

Slag Samples

A composite from each batch of slag (two samples) was analyzed for ≅40 elements by ICP. TCO and gravimetric analyses were conducted on one sample.

SECTION 3

SUMMARY OF RESULTS

This section presents the test results. Operating conditions, sampling trains, and results of process sample analysis are also presented.

3.1 SAMPLING PROTOCOL

Table 3-1 summarizes general information regarding the test runs (slag batch number, quench water code, and desired temperature code). The following code is used on subsequent tables: ASTM Type I quench water, A; blast furnace blowdown quench water, B; coke plant quench water, C; 593°C (1100°F) slag temperature, L; 815°C (1500°F) slag temperature, H.

Table 3-2 summarizes pertinent test run data (for two groups) including furnace temperature, slag temperature at two depths, volume of quench water applied and recovered, test time, and volume of dry gas sampled. A major part of the applied water was recovered. Some of the steam would escape between the hood and slag pot. In each test run for the first group a SASS sampling train, an ammonia sampling train, and a Method 13B sampling train were operated. A test run was conducted in one day with the use of one slag pot. The first set of six runs was completed between January 31 and February 15, 1984. The second group of 6 runs was a retest conducted between April 2 and April 19, 1984. In the retest only the SASS sampling train was operated. The retest was conducted because the particulate data obtained in the first series were suspect.

3.2 PARTICULATE EMISSIONS

Table 3-3 summarizes the results obtained for particulate emissions for the second series of SASS test runs. The data obtained for low-temperature and high-temperature slag quench with ASTM Type I, blast furnace blowdown, and coke plant water are presented.

TABLE 3-1. SUMMARY OF SLAG PIT TEST RUNS

(First Group)

Run No.	Slag batch	Quench water		Desired slag temperature		
		Type	[code]	°C	(°F)	[code]
1	1	ASTM Type I	[A]	593	(1100)	[L]
2	1	ASTM Type I	[A]	815	(1500)	[H]
3	1	Blast furnace blowdown	[B]	593	(1100)	[L]
4	2	Blast furnace blowdown	[B]	815	(1500)	[H]
5	2	Coke plant	[C]	593	(1100)	[L]
6	2	Coke plant	[C]	815	(1500)	[H]

NOTE: Run 1 to 6 consisted of a SASS test run, a Method 13B test run, and an ammonia test run.

(Second Group)

Run No.	Slag batch	Quench water		Desired slag temperature		
		Type	[code]	°C	(°F)	[code]
RT-1	3	ASTM Type I	[A]	593	(1100)	[L]
RT-2	3	ASTM Type I	[A]	815	(1500)	[H]
RT-3	3	Blast furnace blowdown	[B]	593	(1100)	[L]
RT-4	4	Blast furnace blowdown	[B]	815	(1500)	[H]
RT-5	4	Coke plant	[C]	593	(1100)	[L]
RT-6	4	Coke plant	[C]	815	(1500)	[H]

NOTE: RT-1 to RT-6 consisted of only a SASS test run.

TABLE 3-2. SUMMARY OF SLAG FURNACE, QUENCH WATER, AND SAMPLING TRAIN CONDITIONS

(First Group)

Test No.	Sampling train I.D.	Average temperature, °C (°F)			Quench water volume, liters		Test time, min	Volume of dry gas sampled	
		Furnace	Slag		Applied	Recovered		Nm^3[a]	dscf[b]
			Deep	Shallow					
	SASS	859 (1579)	596 (1105)	596 (1105)	10.0	9.4	320	12.85	453.94
1	NH3	863 (1585)	609 (1129)	580 (1076)			104	3.76	132.82
AL					9.4	7.9			
	13B	887 (1629)	620 (1148)	597 (1107)			112	3.11	109.91
	SASS	987 (1809)	823 (1514)	784 (1443)	10.0	8.9	250	7.74	273.45
2	NH3	994 (1822)	826 (1519)	799 (1471)			105	2.43	85.79
AH					9.8	9.0			
	13B	989 (1812)	834 (1534)	800 (1472)			135	3.04	107.21
	SASS	902 (1656)	606 (1123)	596 (1105)	10.0	8.6	240	5.29	186.71
3	NH3	919 (1687)	603 (1118)	605 (1122)			120	2.63	92.94
BL					10.0	8.6			
	13B	882 (1620)	602 (1116)	589 (1093)			120	1.95	68.97
	SASS	991 (1816)	825 (1518)	833 (1531)	10.0	9.1	240	6.50	229.45
4	NH3	955 (1751)	804 (1480)	798 (1468)			120	3.18	112.42
BH					7.7	4.7			
	13B	969 (1776)	831 (1528)	819 (1506)			120	0.73	25.83
	SASS	865 (1589)	606 (1123)	595 (1104)	10.0	8.1	240	6.83	241.20
5	NH3	854 (1569)	603 (1118)	609 (1128)			120	3.37	119.11
CL					10.0	8.6			
	13B	808 (1486)	613 (1136)	596 (1105)			120	1.56	55.23
	SASS	1087 (1988)	790 (1454)	792 (1458)	10.0	7.3	340	5.91	208.55
6	NH3	>1093 (>2000)	825 (1517)	809 (1489)			120	3.37	118.86
CH					10.0	6.5			
	13B	>1093 (>2000)	822 (1511)	815 (1500)			135	0.72	25.50

(continued)

Table 3-2 (continued)

(Second Group)

Test No.	Sampling train I.D.	Average temperature, °C (°F)			Quench water volume, liters		Test time, min	Volume of dry gas sampled	
		Furnace	Slag						
			Deep	Shallow	Applied	Recovered		Nm^3[a]	dscf[b]
RT-1 AL	SASS	N/A[c]	598 (1108)	600 (1112)	10.0	7.9	260	5.44	192.10
RT-2 AH	SASS	N/A	847 (1556)	812 (1493)	10.0	9.2	240	4.59	162.26
RT-3 BL	SASS	N/A	604 (1120)	587 (1089)	10.0	7.5	240	2.26	79.69
RT-4 BH	SASS	N/A	922 (1691)	814 (1498)	10.0	8.6	240	3.36	118.64
RT-5 CL	SASS	N/A	705 (1302)	589 (1093)	10.0	9.1	240	4.85	171.13
RT-6 CH	SASS	N/A	941 (1725)	810 (1490)	10.0	N/A	240	5.45	192.37

[a] Dry normal cubic meter.
[b] Dry standard cubic feet.
[c] Not available.

TABLE 3-3. SUMMARY OF PARTICULATE EMISSIONS AS DETERMINED FROM SASS TEST RUNS

(Second Group)

Test run no.	Code	Volume of gas sampled, Nm^3	Volume of quench water, liters		Filterable Particulate		
			Applied	Recovered	mg	mg/Nm^3	Mg/liter quench water applied
RT-1	AL	5.44	10.0	7.9	803	147.6	80.3
RT-2	AH	4.59	10.0	9.2	867	188.9	86.7
RT-3	BL	2.26	10.0	7.6	2772	1226.5	277.2
RT-4	BH	3.36	10.0	8.6	2715	808.0	271.5
RT-5	CL	4.85	10.0	9.1	1570	323.7	157.0
RT-6	CH	5.45	10.0	N/A	1928	353.8	192.8

N/A Not Available.

3.3 SULFUR DIOXIDE EMISSIONS

Table 3-4 summarizes the results obtained by using the barium thorin titration method to analyze SO_2 emissions in the SASS train condensate catch and hydrogen peroxide impinger. Over the entire test series, SO_2 emissions ranged from 75.8 to 1312 mg/liter of quench water applied.

3.4 SELECTED METALS EMISSIONS

Table 3-5 summarizes the results obtained from an ICP analysis of SASS samples for metals (second series of six runs). The major elements found in all samples were aluminum, calcium, sodium, and silicon.

3.5 ORGANIC EMISSIONS

Table 3-6 summarizes the results of the gravimetric organic analysis conducted on samples in all SASS runs. Level 1 procedures were followed. Both filterable and condensible organics were determined.

Table 3-7 summarizes the priority pollutants that were found in any one sample by quantitative GC/MS analysis. The amount of each compound is reported as total micrograms (µg) and as µg per liter of quench water applied (µg/liter). All pesticides were excluded. Table 3-8 lists the priority pollutants that were not found in any SASS train sample. Table 3-9 summarizes the results of the total organic carbon analysis (C_7 - C_{16}) as determined from the SASS train. This table presents the mass of organic carbon per specific chain length and the total mass of all organic carbon within the C_7 - C_{16} range and above C_{16}.

3.6 GASEOUS TEST RESULTS

Table 3-10 summarizes the results obtained from sampling the steam that was evolved by the slag quench for cyanide, chloride, and fluoride. Cyanide emissions ranged from <0.016 to 4.7 mg/liter of quench water applied; chloride emissions ranged from 5.8 to 792.4 mg/liter of quench water applied; and fluoride emissions ranged from 59.7 to 112.5 mg/liter of quench water applied. The amount of these pollutants evolved generally increased with slag temperature. In addition, emissions during blast furnace water quenching were higher than emissions during ASTM Type 1 water quenching, and coke plant water quenching was higher than blast furnace water quenching.

TABLE 3-4. SUMMARY OF SULFUR DIOXIDE EMISSIONS FOUND IN SASS TRAIN SAMPLES

(First Group)

Run No.	Code	Volume of gas sampled, Nm^3	Volume of quench water, liters		Sulfur dioxide content		
			Applied	Recovered	mg	mg/Nm^3	mg/liter of quench water applied
1	AL	12.85	10.0	9.4	1,652	128.6	165.2
2	AH	7.74	10.0	8.9	3,343	431.9	334.3
3	BL	5.29	10.0	8.6	2,548	481.7	254.8
4	BH	6.50	10.0	9.1	758	116.6	75.8
5	CL	6.83	10.0	8.1	2,685	393.1	268.5
6	CH	5.91	10.0	7.3	13,120	2,220.0	1,312.0

(Second Group)

Run No.	Code	Volume of gas sampled, Nm^3	Volume of quench water, liters		Sulfur dioxide content		
			Applied	Recovered	mg	mg/Nm^3	mg/liter of quench water applied
RT-1	AL	5.44	10.0	7.9	3,775	693.9	377.5
RT-2	AH	4.59	10.0	9.2	4,088	890.6	408.8
RT-3	BL	2.26	10.0	7.5	3,454	1,528.3	345.4
RT-4	BH	3.36	10.0	8.6	3,417	1,017.0	341.7
RT-5	CL	4.85	10.0	9.1	4,885	1,007.2	488.5
RT-6	CH	5.45	10.0	N/A	12,010	2,203.7	1,201.0

N/A Not Available.

TABLE 3-5. SUMMARY OF SASS ICP ANALYSIS (RETESTS)

Element	ICP											
	RT-1		RT-2		RT-3		RT-4		RT-5		RT-6	
	mg	mg/liter water applied	mg	mg/liter water applied	mg	mg/liter water applied	mg	mg/liter water applied	mg	mg/liter water applied	mg	mg/liter water applied
Aluminum	16	1.6	24	2.4	19	1.9	27	2.7	21	2.1	12	1.2
Antimony	<0.4	<0.04	<0.5	<0.05	<0.4	<0.04	<0.4	<0.04	<0.4	<0.04	<0.5	<0.05
Arsenic	<0.7	<0.07	<0.8	<0.08	<0.7	<0.07	<0.7	<0.07	<0.8	<0.08	<0.8	<0.08
Barium	0.78	<0.078	1.4	0.14	0.76	0.076	1.6	0.16	1.6	0.16	1.5	0.15
Beryllium	<0.01	<0.001	<0.01	<0.001	<0.01	<0.001	<0.01	<0.001	<0.01	<0.001	<0.01	<0.001
Boron	5.6	.56	20	2.0	11	1.1	24	2.4	27	2.7	7.2	0.72
Cadmium	<0.01	<0.001	<0.03	<0.003	<0.03	<0.003	0.20	0.02	<0.03	<0.003	<0.03	<0.003
Calcium	28	2.8	29	2.9	32	3.2	31	3.1	18	1.8	3.6	0.36
Chromium	0.05	0.005	0.06	0.006	11	1.1	0.23	0.023	0.06	0.006	<0.04	<0.004
Cobalt	<0.1	<0.01	<0.08	<0.008	<0.08	<0.008	<0.08	<0.008	<0.08	<0.008	<0.09	<0.009
Copper	<0.01	<0.001	<0.02	<0.002	<0.02	<0.002	<0.02	<0.002	<0.02	<0.002	<0.02	<0.002
Iron	1.7	0.17	2.0	0.20	3.3	0.33	1.4	0.14	1.4	0.14	1.7	0.17
Lead	<1	<0.1	<2	<0.2	<2	<0.2	4	0.4	4	0.4	<2	<0.2
Magnesium	<0.5	<0.05	<0.5	<0.05	<1	<0.1	1	0.1	<0.5	<0.05	<0.5	<0.05
Manganese	0.06	0.006	0.03	0.003	0.1	0.01	0.08	0.008	0.1	0.01	<0.1	<0.01
Mercury	<0.4	<0.04	<0.4	<0.04	<0.4	<0.04	<0.4	<0.04	<0.4	<0.04	<0.5	<0.05
Molybdenum	0.2	0.02	<0.05	<0.005	<0.05	<0.005	0.40	0.04	<0.04	<0.004	<0.05	<0.005
Nickel	0.16	0.016	0.1	0.01	0.34	0.034	0.35	0.035	0.65	0.065	<0.2	<0.02
Phosphorus	<3	<0.3	<3	<0.3	<3	<0.3	<3	<0.3	<3	<0.3	<3	<0.3
Potassium	4	0.4	<1	<0.1	21	2.1	14	1.4	<2	<0.2	<3	<0.3
Selenium	<1	<0.1	<2	<0.2	<1	<0.1	<1	<0.1	<1	<0.1	<2	<0.2
Silicon	120	12.0	210	21.0	84	8.4	210	21.0	210	21.0	190	19.0
Silver	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sodium	22	2.2	35	3.5	26	2.6	46	4.6	38	3.8	33	3.3
Sulfur	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Thallium	<2	<0.2	<2	<0.2	<2	<0.2	<2	<0.2	<2	<0.2	<2	<0.2
Titanium	<0.06	<0.006	<0.07	<0.007	<0.07	<0.007	<0.06	<0.006	<0.07	<0.007	<0.06	<0.006
Vanadium	<0.04	<0.004	<0.05	<0.005	<0.04	<0.004	<0.04	<0.004	<0.04	<0.004	<0.05	<0.005
Zinc	0.41	0.041	0.14	0.014	0.51	0.051	9.8	0.98	8.4	0.84	6.7	0.67

TABLE 3-6. SUMMARY OF GRAVIMETRIC ORGANIC ANALYSIS

Test run No.	Code	Filterable organics		Condensible organics	
		mg	mg/liter of quench water applied	mg	mg/liter of quench water applied
1	AL	30.0	3.0	370	37.0
2	AH	4.0	0.4	352	35.2
3	BL	6.0	0.6	154	15.4
4	BH	4.0	0.4	630	63.0
5	CL	20.0	2.0	865	86.5
6	CH	44.0	4.4	174	17.4
Blank	-	<2.0	-	2	-

Quench water	Organics mg/liter
ASTM Type I	4.5
Blast furnace	6.0
Coke plant	225.0

TABLE 3-7. SUMMARY OF PRIORITY POLLUTANTS FOUND IN ANY SAMPLE ANALYZED BY GC/MS

Compound	ASTM Type I					Blast Furnace Water					Coke Plant water				
	Quench water µg/liter	Low temperature (Run 1)		High temperature (Run 2)		Quench water, µg/liter	Low temperature (Run 3)		High temperature (Run 4)		Quench water, µg/liter[a]	Low temperature (Run 5)		High temperature (Run 6)	
		µg	µg/liter applied	µg	µg/liter applied		µg	µg/liter applied	µg	µg/liter applied		µg	µg/liter applied	µg	µg/liter applied
P-Chloro-M-Cresol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	13,342	1,334.2	ND	ND
2-Chlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	6,349	634.9	ND	ND
2-Nitrophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2,632	263.2	ND	ND
Phenol	ND	70	7.0	200	20	ND	ND	ND	144	14.4	249,000	117,542	11,754.2	68.8	6.9
Benzoic Acid	ND	2,938	293.8	7,990	799	ND	ND	ND	4,680	468.0	ND	7,030	703.0	ND	ND
2-Methylphenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	48,400	50,040	5,004	ND	ND
4-Methylphenol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	18,676	1,867.6	ND	ND
Fluoranthene	ND	1,094	109.4	60	6.0	ND	ND	ND	169	16.9	2,610	8,074	807.4	ND	ND
Napthalene	ND	78	7.8	160	16.0	ND	ND	ND	244	24.4	12,800	24,172	2,417.2	207.6	20.8
N-Nitrosodipropylamine	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Bis(2-Ethylhexyl)phthalate[b]	ND	14,118	1,411	10,346	1,035	ND	5,874	587.4	20,317	2,031.7	ND	95,336	9,533.6	8,815	881.5
Benzylbutyl Phthalate[b]	ND	7,306	730.6	ND	ND	ND	4,000	400.0	25,000	2,500.0	ND	17,858	1,785.8	6,292	629.2
Di-N-Butyl Phthalate	ND	46	4.6	42	4	ND	74	7.4	ND	ND	90	ND	ND	ND	ND
Di-N-Octyl Phthalate	ND	9,544	954.4	7,199	719.9	ND	5,563	556.3	1,264	126.4	ND	10,681	1,068.1	8,040	804.0
Diethyl Phthalate	ND	ND	ND	334	33.4	ND	378	37.8	2,632	263.2	ND	ND	ND	96	9.6
Dimethyl Phthalate	ND	ND	ND	22	2.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Chrysene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1,040	1,800	180.0	ND	ND
Acenaphthylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3,420	5,348	534.8	ND	ND
Anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2,280	2,660	266.0	ND	ND
Phenanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4,880	10,976	1,097.6	ND	ND
Pyrene	ND	305	30.5	144	14.4	ND	ND	ND	478	47.8	1,900	4,480	448.0	ND	ND
4-Chloroaniline	ND	59	5.9	122	12.2	ND	ND	ND	188	18.8	34,300	ND	ND	ND	ND
Dibenzofuran	ND	ND	ND	ND	ND	ND	ND	ND	44	4.4	1,630	8,676	867.6	40	4.0
2-Methylnapthalene	ND	ND	ND	65	6.5	ND	ND	ND	89	8.9	5,850	10,630	1,063.0	ND	ND

[a] In addition to the compounds listed in this table, the following were present in coke plant quench water in mg/liter: 2-4 dimethylphenol - 9,720; Acenaphthene - 280; Benzo(a)anthracene - 630; Benzo(a)pyrene - 650; Benzo(b)fluoranthene and/or Benzo(K)fluoranthene - 240; Benzo(ghi)perylene - fluorene - 2,100; dibenzo(a,h)anthracene - 120; Indeno (1,2,3-cd)pyrene - 290.

[b] Front half of SASS train (probe rinse and filter) had blank values of 284 ng bis(2-ethylhexyl) phthalate and 56 ng benzylbutyl phthalate. All other compounds were undetectable in all other blanks including method blanks and XAD-2 blank.

TABLE 3-8. SUMMARY OF COMPOUNDS NOT FOUND IN ANY SAMPLE WHEN ANALYZED BY GC/MS FOR PRIORITY POLLUTANTS EXCLUDING PESTICIDES

2,4,6-Trichlorophenol	Hexachlorocyclopentadiene
2,4-Dichlorophenol	Isophorone
4-Nitrophenol	Nitrobenzene
4,6-Dinitro-O-Cresol	N-Nitrosodiphenylamine
Pentachlorophenol	Dibenzo(AH)Anthracene
2,4,5-Trichlorophenol	Aniline
Benzidine	Benzyl Alcohol
1,2,4-Trichlorobenzene	2-Nitroaniline
Hexachlorobenzene	3-Nitroaniline
Hexachloroethane	4-Nitroaniline
Bis(2-Chloroethyl)Ether	2-Chloronaphthalene
1,2-Dichlorobenzene	1,3-Dichlorobenzene
1,4-Dichlorobenzene	3,3'Dichlorobenzidine
2,4-Dinitrotoluene	2,6-Dinitrotoluene
1,2-Diphenylhydrazine	4-Bromphenylphenylether
Bis(2-Chloroisopropyl)Ether	Bis(2-Chlorethoxy)Methane
Hexachlorobutadiene	

TABLE 3-9. SUMMARY OF RESULTS OF ORGANIC CARBON ANALYSIS (C_7-C_{16}) AS DETERMINED BY SASS TEST RUNS

Test run I.D.	Volume of quench water, liters applied	Mass of organic carbon per chain length, mg									C_{16} and above	Total organic carbon C_7-C_{16} and above	
		C_7-C_8	C_8-C_9	C_9-C_{10}	C_{10}-C_{11}	C_{11}-C_{12}	C_{12}-C_{13}	C_{13}-C_{14}	C_{14}-C_{15}	C_{15}-C_{16}		mg	mg/liter of quench water applied
AL	10	0.48	0.22	5.8	8.8	1.1	3.2	0.24	2.0	1.1	5.9	28.8	2.88
AH	10	10.8	0.66	1.0	4.0	2.3	3.6	2.0	0.66	0.84	0.74	26.6	2.66
BL	10	0.90	3.0	0.64	1.1	0.88	1.8	0.54	0.20	0.42	20.9	30.4	3.04
BH	10	11.9	10.5	4.7	13.4	14.2	10.7	3.8	2.4	3.2	5.6	80.4	8.04
CL	10	0.38	5.8	3.7	57.7	21.2	99.0	6.9	10.8	15.8	23.5	244.8	24.48
CH	10	8.7	4.8	2.2	1.6	2.0	2.8	1.7	0.20	1.6	1.3	26.9	2.69
Blank	-	<0.01	2.24[a]	<0.01	0.06	0.01	0.36[b]	0.03	0.07	0.18	0.25	3.20	-

[a] 1.93 mg in acid extract of condensate blank.

[b] 0.29 mg in acid extract of condensate blank.

NOTE: The organic carbon (C_7-C_{16}) analysis may be biased on the higher side because of use of 50/50, acetone/methylene chloride solution for recovery of front half rinses.

TABLE 3-10. SUMMARY OF CYANIDE, CHLORIDE, AND FLUORIDE SAMPLING RESULTS

Run No.	Code	Volume of gas sampled, Nm^3	Volume of quench water applied, liters	Cyanide Content			Chloride Content			Fluoride Content		
				mg	mg/Nm^3	mg/liter of quench water applied	mg	mg/Nm^3	mg/liter of quench water applied	mg	mg/Nm^3	mg/liter of quench water applied
1	AL	3.11	4.7	<0.075	<0.024	<0.016	27.5	8.8	5.8	280.8	90.3	59.7
2	AH	3.04	4.9	<0.089	<0.029	<0.018	31.1	10.2	6.4	505.8	166.4	103.2
3	BL	1.95	5.0	0.095	0.049	0.019	621.2	318.6	124.2	186.7	95.7	37.3
4	BH	0.73	3.8	<0.067	<0.092	<0.018	774.0	1060.3	203.7	231.1	316.6	60.8
5	CL	1.56	5.0	23.4	15.0	4.7	3962	2540	792.4	247.9	158.9	49.6
6	CH	0.72	5.0	20.4	28.3	4.1	3296	4578	659.2	562.5	781.2	112.5

Table 3-11 summarizes the results of the ammonia tests. Ammonia emissions ranged from <0.2 to 530.2 mg/liter of quench water applied. Quenching at the lower slag temperature released more ammonia than quenching at the higher slag temperature. Ammonia emissions were higher during blast furnace water quenching than during ASTM Type I water quenching. Similarly, ammonia emissions were higher during coke plant water quenching than during blast furnace water quenching.

During each SASS run (in the first series of tests) a grab sample of evolved steam and gas was collected in a heated glass bulb. This sample was then analyzed for C_1 through C_7 hydrocarbon by flame ionization detection. Table 3-12 summarizes the results of the analysis. No significant level of C_1 through C_7 hydrocarbons were found in any of the grab samples.

3.7 SLAG AND QUENCH WATER COMPOSITION

A representative sample of each batch of slag was analyzed for metals by ICP analysis. Table 3-13 presents the results of this analysis. Calcium was found to be the largest single constituent.

Table 3-14 presents the results of ICP analysis of the quench water used in both series of tests. Blast furnace blowdown water contained the most potassium. Coke plant water contained the most sulfur. Table 3-15 presents the results of selected miscellaneous analysis conducted on the quench water samples used in both series of tests. Table 3-16 indicates the slag analysis (slag data were supplied by Armco, Inc).

The results of the organic analysis of the quench water are incorporated into the respective tables; i.e., gravimetric analysis is contained in Table 3-6, and GC/MS for priority pollutants is in Table 3-7.

3.8 QUALITY ASSURANCE SUMMARY

All sampling and analysis procedures used are contained in the QAPP prepared for this project. The precision and accuracy of the sampling and analysis are within the limits specified in Section 3 of the QAPP as revised. Any analyses not meeting these limits were reanalyzed according to our SOPs until these limits were obtained.

TABLE 3-11. SUMMARY OF AMMONIA SAMPLING RESULTS

Run No.	Code	Volume of gas sampled, Nm^3	Volume of quench water, liters		Ammonia content		
			Applied	Recovered	mg	mg/Nm^3	mg/liter of quench water applied
1	AL	3.76	4.7	3.9	<2.2	<0.6	<0.5
2	AH	2.43	4.9	4.5	<1.2	<0.5	<0.2
3	BL	2.63	5.0	4.3	106	40.3	21.2
4	BH	3.18	3.8	2.3	46.4	14.6	12.2
5	CL	3.37	5.0	4.3	2651	786.6	530.2
6	CH	3.37	5.0	3.2	711	211.0	142.2

TABLE 3-12. SUMMARY OF C_1 THROUGH C_7 HYDROCARBONS - GRAB SAMPLE ANALYSIS BY FLAME IONIZATION DETECTION (ppm, Volume/Volume)

SASS test run No.	Code	C_1-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-C_6	C_6-C_7	Total
1	AL	1.9	0.9	20.1	10.3	0.9	1.9	36.0
2	AH	1.4	0.5	0.1	2.2	<0.1	<0.1	4.2
3	BL	2.1	0.3	<0.2	4.3	<0.2	<0.3	6.7
4	BH	3.4	0.2	<0.1	11.7	<0.1	<0.1	15.3
5	CL	7.6	0.6	1.9	6.9	0.1	0.3	17.4
6	CH	2.5	0.1	0.3	2.0	<0.1	<0.1	4.9

TABLE 3-13. SUMMARY OF SLAG ICP ANALYSIS

Elements	Units	Batch 1	Batch 2	Batch 3	Batch 4
Aluminum	Percent	4.6	5.1	4.5	4.6
Antimony	µg/g	<3	<3	<3	<3
Arsenic	µg/g	<6	<6	<7	<8
Barium	µg/g	420	490	440	390
Beryllium	µg/g	11	9.1	11	9.8
Boron	µg/g	67	220	81	83
Cadmium	µg/g	9.9	2.7	12	<0.4
Calcium	Percent	36	25	31.0	31.0
Chromium	µg/g	960	230	34	310
Cobalt	µg/g	8.5	8.2	7.3	6.5
Copper	µg/g	<0.02	<0.2	6.8	4.9
Iron	Percent	0.28	1.6	0.12	0.28
Lead	µg/g	<17	<17	17	<16
Magnesium	Percent	7.00	5.5	5.20	6.40
Manganese	Percent	0.54	1.2	0.45	0.38
Mercury	µg/g	<3	<3	<3	<3
Molybdenum	µg/g	4.5	5.5	4200	4.9
Nickel	µg/g	550	25	11	120
Phosphorus	µg/g	<37	49	<26	<36
Potassium	µg/g	0.29	0.63	0.23	0.0
Selenium	µg/g	<8	<8	<8	<8
Silicon	Percent	0.003	0.15	0.27	33
Silver	µg/g	<2	<2	<2	<5
Sodium	Percent	0.25	0.35	0.24	0.15
Sulfur	Percent	1.5	1.00	1.70	2.10
Thallium	µg/g	<9	<9	<10	<10
Titanium	Percent	0.29	0.37	0.35	0.27
Vanadium	µg/g	37	40	30	25
Zinc	µg/g	75	2.2	4.9	2.5

TABLE 3-14. SUMMARY OF QUENCH WATER ICP RESULTS

(First Group)

Element	Units	Quench Water		
		ASTM Type I	Blast furnace blowdown	Coke plant
Aluminum	mg/liter	<0.05	1.1	<0.05
Antimony	mg/liter	<0.05	<0.03	<0.03
Arsenic	mg/liter	<0.06	<0.06	<0.06
Barium	mg/liter	0.15	0.42	0.06
Beryllium	µg/liter	150	1	58
Boron	µg/liter	<9	<9	<9
Cadmium	µg/liter	<2	<2	<2
Calcium	mg/liter	0.11	170	21
Chromium	µg/liter	9	7	13
Cobalt	µg/liter	<6	<6	<6
Copper	µg/liter	15	5	<1
Iron	mg/liter	0.04	6.4	0.87
Lead	mg/liter	<0.08	<0.08	<0.08
Magnesium	mg/liter	<0.04	57	6
Manganese	mg/liter	<0.001	3	0.016
Mercury	mg/liter	<0.03	<0.03	<0.03
Molybdenum	µg/liter	<2	10	2
Nickel	µg/liter	<3	<3	<3
Phosphorus	mg/liter	0.71	<0.18	1.1
Potassium	mg/liter	0.29	13.0	3.1
Selenium	mg/liter	<0.08	<0.08	<0.08
Silicon	mg/liter	0.097	16	1.5
Silver	µg/liter	<2	<2	<2
Sodium	mg/liter	1.2	70	24
Sulfur	mg/liter	0.2	81	800
Thallium	mg/liter	<0.09	<0.09	<0.09
Titanium	µg/liter	13	18	<5
Vanadium	µg/liter	<3	<3	<3
Zinc	µg/liter	<3	4.8	<3

(continued)

Table 3-14 continued

(Second Group)				
		Quench Water		
Element	Units	ASTM Type I	Blast furnace blowdown	Coke plant
Aluminum	mg/liter	<0.05	0.24	<0.05
Antimony	mg/liter	<0.04	<0.04	<0.04
Arsenic	mg/liter	<0.06	<0.06	<0.06
Barium	mg/liter	0.014	0.12	0.038
Beryllium	µg/liter	<0.5	<0.5	<0.5
Boron	µg/liter	20	<9	110
Cadmium	µg/liter	<2	<2	<2
Calcium	mg/liter	<0.05	95	23
Chromium	µg/liter	<1	<1	7
Cobalt	µg/liter	<6	<6	<6
Copper	µg/liter	<1	<1	<1
Iron	mg/liter	0.021	2.0	1.5
Lead	mg/liter	<0.09	<0.09	<0.09
Magnesium	mg/liter	<0.04	48	7.4
Manganese	mg/liter	<0.001	2.0	0.024
Mercury	mg/liter	<0.03	<0.03	<0.03
Molybdenum	µg/liter	<2	<2	<2
Nickel	µg/liter	<3	<3	7
Phosphorus	mg/liter	<0.2	<0.2	<0.2
Potassium	mg/liter	<0.05	340	<0.05
Selenium	mg/liter	<0.09	<0.09	<0.09
Silicon	mg/liter	<0.02	14	1.4
Silver	µg/liter	<2	<2	<2
Sodium	mg/liter	0.27	82	22
Sulfur	mg/liter	<0.03	40	680
Thallium	mg/liter	<0.1	<0.1	<0.1
Titanium	µg/liter	<5	<5	<5
Vanadium	µg/liter	<3	<3	<3
Zinc	µg/liter	<3	3.2	22

TABLE 3-15. SUMMARY OF SELECTED MISCELLANEOUS ANALYSES CONDUCTED ON THE THREE QUENCH WATERS

(First Group)

Parameter	Units	Quench water		
		ASTM Type I	Blast furnace	Coke[a] plant
pH	S.U.	7.79	7.81	8.42
Suspended solids	mg/liter	<2.00	63.00	14.00
Dissolved solids	mg/liter	61.00	1289.00	2519.00
Chloride	mg/liter	<0.30	318.00	1160.00
Fluoride	mg/liter	0.04	8.28	5.13
Ammonia nitrogen	mg/liter	1.30	20.10	683.00
Total Kjeldahl	mg/liter	<0.50	21.00	746.00
Phenolics	mg/liter	<0.05	<0.05	164.00
Total cyanide	mg/liter	<0.02	0.09	2.26

[a]Originally coke plant water had 70 mg/liter of suspended solids and 12,900 mg/liter of dissolved solids. The coke plant water was diluted with ASTM Type I water to the value reported above prior to application on the slag.

(continued)

Table 3-15 (continued)

(Second Group)

Parameter	Units	Quench water		
		ASTM Type I	Blast[b] furnace	Coke[b] plant
pH	S.U.	5.72	7.90	8.81
Suspended solids	mg/liter	<2	17	10
Dissolved solids	mg/liter	29	1305	2637
Chloride	mg/liter	<0.3	199	845
Fluoride	mg/liter	0.20	14.4	4.81
Ammonia nitrogen	mg/liter	<0.5	53.2	727
Total Kjeldahl nitrogen	mg/liter	<0.5	54.0	794
Phenolics	mg/liter	<0.01	0.06	183
Total cyanide	mg/liter	<0.02	0.70	2.89

[b]Original samples were diluted with ASTM Type I water to attain the above indicated TDS levels.

TABLE 3-16. SLAG COMPOSITION
(percentage)

Batch No.	Date sample obtained (1984)	CaO	MgO	Al_2O_3	SiO_2	MnO	S	Basicity
1	1/20	39.35	10.42	8.94	38.08	1.29	1.37	1.058
2	2/09	39.88	8.50	8.26	40.76	1.20	1.26	0.987
3	3/29	39.62	10.10	9.43	37.92	0.61	1.58	1.050
4	4/05	35.57	10.15	9.06	37.24	1.52	1.23	0.987

The major QA problem uncovered during this project was a possible error in our procedure for extracting the particulate and resin obtained from the SASS train samples. We used a 50/50 mixture of methylene chloride and acetone to extract these fractions. It has been reported through the review process that the use of acetone may cause artifact formation and yield high bias to the gravimetric, TCO, and other organic data. These data have been carefully reviewed. The results of the blank analyses performed concurrently with the samples have been added to the data tables for these three analyses. The blank results for the gravimetric analyses are insignificant. No other indication or evaluation of any bias present in these results is possible.

The TCO analyses were reviewed. The results reported in Table 3-9 represent the sum of four individual fractions--probe rinse/filter extract, XAD-2 extract, base/neutral condensate extract, and acid condensate extract. Only the first two fractions are affected by the use of acetone; no acetone was used in the extraction of condensate. The majority (over 80 percent) of the TCO blank was found in the acid extract of the condensate. The blank train value for the TCO analysis represents a maximum of 12 percent for these six SASS runs. Therefore, no significant bias to these data appears to be present.

The results for individual organic compounds were also reviewed. For five of the six runs, between 95 and 100 percent of the reported mass was due to benzoic acid and phthalates. In the remaining sample (Run 5), the other compounds reported were present or are related to compounds present in the quench water. A portion of the phthalates found in the samples was detected in the blank train. The use of acetone to extract the filter and resin should affect the blank as well as the sampler. The amount found in the blanks is insignificant compared with the samples. The high benzoic acid and phthalate concentration is addressed in Section 4.

SECTION 4

EVALUATION OF RESULTS

An evaluation of the test data in terms of water quality, slag temperature during quenching, and slag characteristics is presented under the following subcategories: particulate emissions; SO_2, HCN, ammonia, fluorides, and chlorides; hydrocarbons C_1 to C_7 and C_7 to C_{16}; metals; and organic emissions.

All emissions except C_1-C_7 are expressed in terms of milligrams or micrograms per liter of water evaporated on the slag surface during quenching. In all cases, the water evaporated is the same as the water applied.

Table 4-1 indicates the water application rates during quenching under each condition. No specific efforts were made to control the water application rates, which are expressed in terms of liters per square foot per minute or gallons per square foot per minute. The rate varied between 0.04 and 0.056 gal/ft² per min. The average for the first group was 0.0507 gal/ft² per minute, and 0.055 gal/ft² per minute for the second group, which are close to the 0.05 gal/ft² per min encountered in practice for hard slag quenching.

4.1 PARTICULATE EMISSIONS

Based on the simulated laboratory scale tests, the particulate emissions (front half of the train only) collected using different types of quench water and temperature conditions are as follows:

Type of quench water	TDS content, mg/liter	Average slag temperature, °F	Particulates, mg/liter of water evaporated
ASTM Type I	29	1112	80.3
ASTM Type I	29	1493	86.7
B. F. Blowdown	1305	1089	277.2
B. F. Blowdown	1305	1498	271.5
Coke plant wastewater	2637	1093	157.0
Coke plant wastewater	2637	1490	192.8

TABLE 4-1. QUENCH WATER APPLICATION RATE

(First Group)

Test run	Slag temperature, °F	Duration of test, min	Quench water evaporated, liters	Water application rate	
				liters/ft² per min	gal/ft² per min
SASS 1	1105	320	10.0	0.159	0.042
SASS 2	1443	250	10.0	0.204	0.054
SASS 3	1105	240	10.0	0.213	0.056
SASS 4	1531	240	10.0	0.213	0.056
SASS 5	1104	240	10.0	0.213	0.056
SASS 6	1458	340	10.0	0.150	0.040

(Second Group)

Test run	Slag temperature, °F	Duration of test, min	Quench water evaporated, liters	Water application rate	
				liters/ft² per min	gal/ft² per min
SASS RT-1	1112	260	10.0	0.196	0.052
SASS RT-2	1493	240	10.0	0.213	0.056
SASS RT-3	1089	240	10.0	0.213	0.056
SASS RT-4	1498	240	10.0	0.213	0.056
SASS RT-5	1093	240	10.0	0.213	0.056
SASS RT-6	1490	240	10.0	0.213	0.056

Note: The total slag surface in the pot is 1.227 ft². The effective quench area was 6 inches in diameter (0.196 ft²) as determined by visual examination of slag surface after each quench. The effective quench area was greyish-white in color.

Table 4-2 is a composite of the current data and the data obtained during fall 1982, when similar simulated laboratory scale tests were conducted using well water and BF blowdown water as the quenching medium.[1]

Based on the information in Table 4-2, it is apparent that for a comparable TDS content of coke plant wastewater (2637 mg/liter) the particulate emissions are approximately 50 percent lower than for an equivalent BF blowdown water (TDS-2491 mg/liter) at high-temperature slag quench. This result is expected because the species of pollutants present in the two types of water are different, and in coke plant water the pollutants break down at high temperatures.

A data set consisting of eight pairs of responses was analyzed. Each pair consisted of a particulate measurement obtained at low temperature plus one obtained at high temperature. The set is further categorized according to the concentration of dissolved solids in the quenching water. There are three pairs of measurements at low concentration and five pairs of measurements at high concentration.

DATA SET USED IN ANALYSIS

Dissolved solids	Particulate concentration	
	Low temp.	High temp.
Low	80.3	86.7
Low	23.1	27.8
Low	25.1	75.2
High	277.2	271.5
High	183.8	392.6
High	151.3	371.8
High	133.7	415.3
High	157.0	192.8

The data were tested for differences between group means based on standard tests. Tail probabilities for these tests are not greatly affected by moderate departures from normality except in the case of small samples. The standard two-sample t test is also based on the assumption that the two sets of random variables are independent. The assumption of independence is in question, but we decided to proceed with the standard two-sample t test because of its widespread use and application. To protect against the assumption of normality, the nonparametric Wilcoxon rank-sum test, based on the independence of the two sets of random variables, was conducted.

TABLE 4-2. PARTICULATE EMISSIONS FROM QUENCHING OF BLAST FURNACE SLAG WITH CONTAMINATED WATER

Type of quench water	TDS content mg/liter	Particulate emissions, mg/liter of quench water applied and evaporated	
		Low-temperature quench (≅1100°F)	High-temperature quench (≅1500°F)
ASTM Type I	29	80.3	86.7
Well water	450	23.1	27.8
	450	25.1	75.2
	450	55.9	
B. F. blowdown (moderate recirculation)	1305	277.2	271.5
B. F. blowdown (high recirculation)	2491	133.7	377.8
	2491	151.3	392.6
	2491	183.8	415.3
Coke plant waste water (diluted with ASTM Type I)	2637	157.0	192.8

A second battery of tests was conducted, both parametric and nonparametric, which was based on the concept of repeated measurements, possibly under altered conditions, on the same experimental unit. For the purposes of this experiment the unit consisted of the water sample used for quenching, with a known concentration of dissolved solids. A pair of observations was obtained, one at low temperature, one at high temperature, based on one sample of water. Three paired-comparison tests were carried out. They consisted of a one-sample t test on the paired differences, plus two nonparametric tests (the sign test, and the signed-rank test). The assumption of normality was required for the one-sample test, but it was not required fo the two nonparametric tests.

Finally, standard two-sample t tests were conducted, within each temperature stratum, for differences between means selected by dissolved solids classifications. In this case the assumption of independence was definitely appropriate. Following are brief summaries of various statistical tests performed on the data.

1. Standard t Test

The measurements obtained at low and high temperatures are assumed to be independent.

a. The population variances in the low temperature and high temperature groups are assumed to be equal. The variance estimate is then obtained by pooling the variance estimates of the two groups. The tail probability is 0.1309 on 14 degrees of freedom (16 - 2 = 14).

b. The population variances in the low temperature and high temperature groups are assumed to be unequal. The variance in each group is estimated separately. The tail probability is 0.1373 on 10.8 degrees of freedom.

2. Levene's Test for Equality of Variances

The tail probability is 0.0263 on 1 and 14 degrees of freedom.

3. Wilcoxon's Rank Sum Test

The difference between the rank sums is computed. The tail probability is 0.1722 based on the CHI-SQUARED distribution on 1 degree of freedom; the Mann-Whitney test statistic yields, as it must, the same tail probability.

4. Correlation

The Pearson product-moment sample correlation coefficient for the low temperature and high temperature measurements yields the value 0.674.

5. Paired Comparisons

Each pair of measurements is assumed to constitute a repeated measurement, under altered conditions, on the same unit. Three tests are available: 1) the one-sample t test on the mean of the (paired) differences; 2) the nonparametric sign test; and 3) the nonparametric signed-rank test. The tail probabilities are, respectively, 0.0453 (on 7 degrees of freedom), 0.0703, and 0.0251.

The paired comparison one-sample t test was repeated on the logarithm of the paired differences. The tail probability was 0.009 on 6 degrees of freedom.

6. Comparison of Group Means According to Level of Dissolved Solids Within the High-Temperature, Low-Temperature Classifications

The assumption of independence is reasonable here.

a. The variances are estimated separately. The tail probabilities are 0.0048 (6 degrees of freedom) for the low-temperature classification and 0.0018 (5.2 degrees of freedom) for the high-temperature classification.

b. The variance estimates are pooled. The tail probabilities are 0.0094 (6 degrees of freedom) for the low-temperature classification and 0.0037 (6 degrees of freedom) for the high-temperature classification.

The measurements in the low-temperature and high-temperature groups should be regarded as repeated measurements on a single unit. The identity of the unit is based, in part, on the amount of dissolved solids. The paired differences are significant. Temperature has a significant effect on the observed particulate concentrations. Within each temperature classification, mean differences based on the concentration of dissolved solids were significant. The concentration of dissolved solids also has a significant effect on the observed particulate concentrations.

In addition, simple correlation and regression analyses were performed for the test data. The coke plant water tests were excluded from this analysis because of the completely different nature of the water, ie., much higher organic contents. The data show the following:

	Low temperature	High temperature
Correlation coefficient	0.603	0.9669
Slope	0.0495	0.14779
Intercept	53.5	30.38

The estimated regression lines for low temperature (1100°F) and high temperature (1500°F) are as follows:

$$y = 53.5 + 0.0495\ x \text{ (for low temperature)}$$

and $$y = 30.38 + 0.14779\ x \text{ (for high temperature)}$$

where x is the TDS content of the quench water (mg/liter) and y is the particulate emissions (mg/liter of quench water evaporated).

Figure 4-1 shows the relationship between particulate emissions, the TDS of quench water, and slag temperature. The high-temperature and low-temperature estimated regression lines (excluding coke plant wastewater data) and 95 percent confidence limits (dotted lines) for both high- and low-temperature quench are indicated. The high-temperature data correlation coefficient is 0.9669 and the spread for the 95 percent confidence limit is narrow compared with the low-temperature data which has a lower correlation coefficient of 0.603. The noise level in the data (due to many variables affecting quenching) is high at the lower temperature range as expected because the effect of other variables overhelms the quench water effect.

It is apparent that a high amount of TDS in the quench water and a high temperature during the quench will yield high particulate emissions.

Visual examination of the inside surface of the collection hood showed discoloration and fine deposits. Before every test run, the inside of the hood was cleaned. One sample of this deposit was tested by ICP for the presence of metals. The ICP results showed a predominant presence of calcium, iron, sodium, and sulfur. The deposits may contain both adhered slag particles and corrosion products from the hood material. No attempt was made to recover these deposits, part of which probably would have become additional particulates had they not adhered to the hood. Those found in the closed hood might be considered to compensate for carryover of particulates with runoff water that would normally occur during normal hard slag quench operations. Also, less material may have condensed on the hot hood at high slag temperature. This problem of deposits inside the hood would also be encountered in actual field tests.

Emission Factor Calculations

Based on the data presented in Table 4-2 and the regression line equations discussed earlier, the emission factor for quenching hard slag at low slag

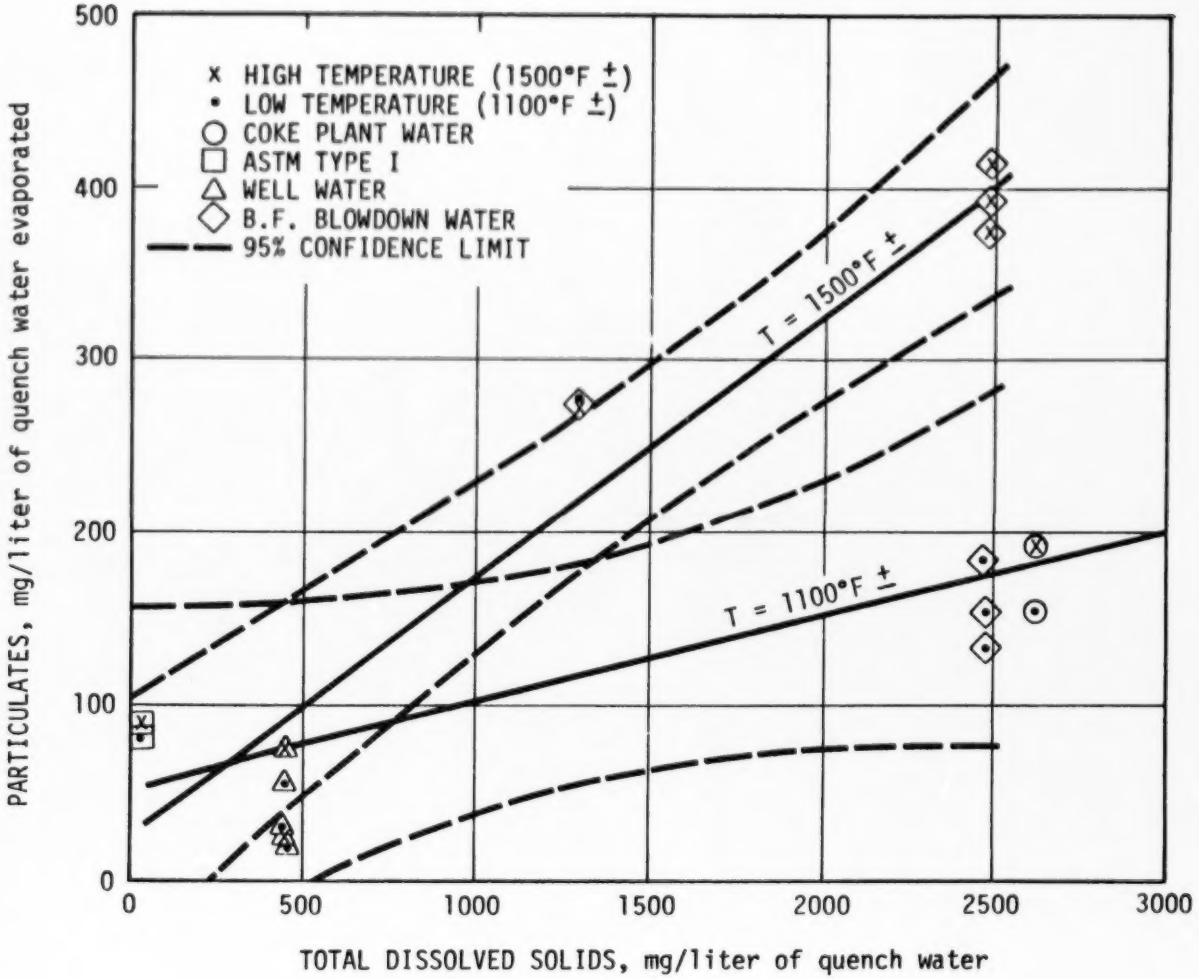


Figure 4-1. Particulate emissions vs. total dissolved solids in quench water.

temperature with quench water (TDS = 2500 mg/liter) is calculated as follows:

$$\text{Emission factor} = \frac{14.5(\text{gal/ton}) \times 3.785(\text{liters/gal}) \times 177.25(\text{mg/liter})}{1000(\text{mg/g}) \times 454(\text{g/lb})}$$

$$= 0.021 \text{ lb/ton of hot metal}$$

where 14.5 gal is the quench water evaporated during hard slag quench (at low temperature) per ton of hot metal.[1]

177.25 mg/liter is the calculated particulate emissions at low-temperature slag quench for a TDS content of 2500 mg/liter using the regression line equation for low temperature.

The emission factor for quenching hard slag at higher slag temperature with quench water (TDS = 2500 mg/liter) is calculated as follows:

$$\text{Emission factor} = \frac{12.47(\text{gal/ton}) \times 3.785(\text{liter/gal}) \times 399.86(\text{mg/liter})}{1000(\text{mg/g}) \times 454(\text{g/lb})}$$

$$= 0.042 \text{ lb/ton of hot metal.}$$

where 12.47 gal is the quench water evaporated during hard slag quench (at high temperature) per ton of hot metal.[1]

399.86 mg/liter is the calculated particulate emissions at high-temperature slag quench for a TDS content of 2500 mg/liter using the regression line equation for high temperature.

4.2 SULFUR DIOXIDE, HCN, AMMONIA, FLUORIDES, AND CHLORIDES

Sulfur Dioxide (SO_2)

Sulfur dioxide data were collected during all six SASS train runs in the first and second groups. The resulting data are as follows:

(First Group)

Type of water	Slag temperature, °F	Slag sulfur content, %	Sulfur in water sample, mg/liter	SO_2 emissions, mg/liter
ASTM Type I	1105	1.37	0.2	165.2
ASTM Type I	1443	1.37	0.2	334.3
BF blowdown	1105	1.37	81.0	254.8
BF blowdown	1531	1.26	81.0	75.8
Coke plant wastewater	1104	1.26	800.0	268.5
Coke plant wastewater	1458	1.26	800.0	1312.0

(Second Group)

Type of water	Slag temperature, °F	Slag sulfur content, %	Sulfur in water sample, mg/liter	SO_2 emissions, mg/liter
ASTM Type I	1112	1.58	<0.03	377.5
ASTM Type I	1493	1.58	<0.03	408.8
BF blowdown	1089	1.58	40	345.4
BF blowdown	1498	1.23	40	341.4
Coke plant wastewater	1093	1.23	680	488.5
Coke plant wastewater	1490	1.23	680	1201

The SO_2 content of the emissions does not show any definite relationship to water quality, slag sulfur content, or quench temperature.

Hydrogen Cyanide (HCN)

The HCN test data are as follows:

Type of water	Slag temperature, °F	Total cyanides in water sample, mg/liter	Total cyanide, mg/liter
ASTM Type I water	1107	<0.02	<0.016
ASTM Type I water	1472	<0.02	<0.018
BF blowdown water	1093	0.09	0.019
BF blowdown water	1506	0.09	<0.018
Coke plant wastewater	1105	2.26	4.700
Coke plant wastewater	1500	2.26	4.100

The total cyanide data indicate cyanide dissociation at both low- and high-temperature slag quench for BF blowdown water.

Ammonia

The ammonia test data are as follows:

Type of water	Slag temperature, °F	Ammonia (N) in water, mg/liter	Ammonia, mg/liter
ASTM Type I water	1076	1.3	<0.5
ASTM Type I water	1471	1.3	<0.2
BF blowdown water	1122	20.1	21.2
BF blowdown water	1468	20.1	12.2
Coke plant wastewater	1128	683	530.2
Coke plant wastewater	1489	683	142.2

The ammonia appears to dissociate at higher temperatures. The ammonia emissions tended to be higher when the quench water contained higher ammonia concentrations.

Fluoride

The fluoride test data are as follows:

Type of water	Slag temperature, °F	Fluorides in water, mg/liter	Fluorides, mg/liter
ASTM Type 1 water	1107	0.04	59.7
ASTM Type I water	1472	0.04	103.2
BF blowdown water	1093	8.28	37.3
BF blowdown water	1506	8.28	60.8
Coke plant wastewater	1105	5.13	49.6
Coke plant wastewater	1500	5.13	112.5

Quenching of higher temperature slag appears to increase total emissions regardless of water quality and the total fluoride content. Most of the metallic fluorides (e.g., ZnF and KF) are highly soluble in water. Because there is no run-off water in these tests, the fluorides content in emissions in these tests may be higher than would be the case during actual operations.

Chlorides

The chloride test data are as follows:

Type of water	Slag temperature, °F	Chlorides in water, mg/liter	Chlorides, mg/liter
ASTM Type I water	1107	<0.3	5.8
ASTM Type I water	1472	<0.3	6.4
BF blowdown water	1093	318.0	124.2
BF blowdown water	1506	318.0	203.7
Coke plant wastewater	1105	1160.0	792.4
Coke plant wastewater	1500	1160.0	659.2

The chloride emissions are higher at high-temperature slag quench (except for coke plant water quench). The chloride emissions are higher if the quench water contained higher chloride concentration.

4.3 HYDROCARBONS AND ORGANIC CARBON

Grab samples were taken for each test run and analyzed for hydrocarbons C_1 through C_7. The values of C_1 thorugh C_7 (total) varied from 4.2 ppm to 36.0 ppm. The evolution of C_1 through C_7 did not show any relationship to quench water or slag temperature.

The analysis of organic carbons (C_7 - C_{16}) determined from SASS test runs was presented earlier in Table 3-9. A 50/50 solution of methylene chloride and acetone was used for recovery of front-half rinses. It appears that use of acetone in this procedure is likely to generate some contamination. However, from Table 3-9, it is apparent that the total organic carbons per liter of water applied are small even with suspected contamination. The true values could be lower than what are shown in Table 3-9. Total organics per liter of water applied did not show any relationship to quench water type or slag temperature in ASTM Type I and BF blowdown water. In coke plant water, however, the organics appear to break down at higher quench temperature.

4.4 METALS

The data for 29 metals analyzed by ICAP under the different test conditions were presented in Table 3-5. In general the tendency is toward higher emissions of aluminum, calcium, potassium, sodium, silicon, and boron with higher slag temperatures, which corresponds with particulate emissions.

4.5 ORGANICS

The quantitative data on priority pollutants (except pesticides) were presented in Table 3-7. Both ASTM Type I water and BF blowdown water did not contain any of the priority pollutants. Selected runs, however, showed the presence of the following in the emissions collected.

	ASTM Type I water	BF blowdown water
Phenol	2 out of 2 samples	1 out of 2 samples
Benzoic acid	2 out of 2 samples	0 out of 2 samples
Fluroanthene	2 out of 2 samples	1 out of 2 samples
Naphthalene	2 out of 2 samples	1 out of 2 samples
Bis(2-ethylhexyl) phthalate	2 out of 2 samples	2 out of 2 samples
Benzyl butyl phthalate	1 out of 2 samples	2 out of 2 samples

	ASTM Type I water	BF blowdown water
Di-N-butyl phthalate	2 out of 2 samples	1 out of 2 samples
Di-N-octyl phthalate	2 out of 2 samples	2 out of 2 samples
Diethyl phthalate	1 out of 2 samples	2 out of 2 samples
Dimethyl phthalate	1 out of 2 samples	0 out of 2 samples
Pyrene	2 out of 2 samples	1 out of 2 samples
4-chloroaniline	2 out of 2 samples	1 out of 2 samples
Dibenzofuran	0 out of 2 samples	1 out of 2 samples
2-methyl naphthalene	1 out of 2 samples	1 out of 2 samples

The levels of benzoic acid and phthalates were relatively high compared with other organic substances, and they bear no definite relationship to quench water quality or slag temperature. Generally benzoic acid is an XAD-2 contaminant. The presence of phthalates is presumably due to binders present in the sampling train filter and/or filter holder gaskets. The formation of other organics may result from slag water reactions at high temperatures in an oxygen-deficient atmosphere. Pyrene is emitted during low-temperature quenching, but it is destroyed during high-temperature quenching. It is not uncommon for unburnt coke to be present in slag, which might contribute the required carbon.

The coke plant wastewater, which was diluted to ±2500 mg/liter, contained many priority pollutants. (Refer to Table 3-7). However, both low- and high-temperature slag quench emissions did not show the presence of 12 priority pollutants that were initially present in the quench water. Eight priority pollutants not initially present in the coke plant wastewater appeared in the slag quench air samples. In general, emissions at higher temperature slag quench showed relatively low priority pollutant emissions, which indicated a breakdown of the pollutants at higher temperatures.

SECTION 5

CONCLUSIONS AND RECOMMENDATIONS

This section presents the major findings and conclusions of this Level 1 laboratory-scale assessment of simulated blast furnace slag quenching with ASTM Type I water, blast furnace blowdown water, and coke plant wastewater diluted to ≈2500 mg/liter of TDS.

5.1 CONCLUSIONS

1. Particulate emissions, as measured by the front half of the modified SASS train during blast furnace slag quenching, increase with increasing slag temperature. The higher the TDS in the quench water, the more pronounced the increase becomes.

   The estimated regression line equations for low and high slag temperature quench are as follows:

   $$y = 53.5 + 0.0495\ x \quad \text{(for low temperature} \cong 1100°F\text{)}$$
   $$y = 30.38 + 0.14779\ x \quad \text{(for high temperature} \cong 1500°F\text{)}$$

   where, x is the TDS content of the quench water and y is the particulate emissions (mg/liter of quench water evaporated).

2. Based on this laboratory-scale simulation, for coke plant wastewater containing a comparable TDS content as that of BF blowdown water, the emissions generated during slag quenching at high temperature are considerably less using coke plant water than when using BF blowdown water. The pollutants present in the coke plant water appear to break down at high-temperature slag quenching and result in less particulate emissions.

3. Emissions of metals increase with high-temperature slag quenching.

4. No specific relationship was found between organic pollutants and the use of ASTM Type I water or BF blowdown water, and slag temperature during quenching.

   Significant amounts of priority pollutants were dissociated from the coke plant wastewater at both low- and high-temperature slag quenching, when all the applied water was evaporated.

5. No correlation was found between quench water quality, slag temperature, or slag sulfur content and emissions of SO_2.

6. Chloride emissions are higher at high-temperature slag quench. The emissions are higher if the quench water contains higher chloride concentration.

7. Cyanides appear to dissociate at both low- and high-temperature slag quenching with BF blowdown water.

8. Ammonia appears to break down at higher-temperature quenching. The ammonia emissions are higher if the quench water contains higher ammonia concentrations.

9. Fluoride emissions are higher at higher-temperature slag quenching and they bear no relationship to the quench water quality.

5.2 RECOMMENDATIONS

It is recommended that the test data and findings of this project be verified by tests conducted at a suitable plant site that practices hard slag quenching with mill service water, blast furnace blowdown water, and, if possible, coke plant wastewater.

SECTION 6

REFERENCES

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